DIELECTRIC PROPERTIES OF POLYMER ELECTROLYTE

Thesis submitted for the Award of degree of

Master of Science

by

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Under the Academic Autonomy

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DECLARATION

I hereby declare that the work carried out in this thesis is entirely original. It was carried out by me along with Miss Pallavi Suhasinee Behera at Department of Physics, National Institute of Technology Rourkela. I further declare that it has not formed the basis for the award of any degree, diploma, or similar title of any university or institution.

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CERTIFICATE

This is to certify that the thesis entitled "**Dielectric properties of Polymer Electrolyte**" being submitted by Miss **Saritarani Maharaj** in partial fulfillment of the requirements for the award of the degree of Master of Science in Physics at National Institute of Technology, Rourkela is an authentic experimental work carried out by her under our supervision. To the best of our knowledge, the experimental matter embodied in the thesis has not been submitted to any other University/Institute for the award of any degree or diploma.

Dr. Dillip Kumar Pradhan

Dr. Sidhartha Jena

ACKNOWLEDGEMENTS

I am obliged to my supervisors Dr. Dillip Kumar Pradhan and Dr. Sidhartha Jena for their continuous guidance and motivation during the entire course of my project. I truly appreciate and value their esteemed guidance and encouragement. I am indebted to them for helping me in defining the problem, providing insights to the solution and ultimately guiding me to bring the thesis into present shape. I would also take the opportunity to express my deepest gratitude to Mr. Tapabrata Dam, Mr. Satyanarayan Tripathy, and Miss Santripti Khandai for their necessary help and cooperation. I also like to thank all the faculty members, all PhD, M Tech(R) scholars and all members of the Department of Physics, N.I.T., Rourkela for their suggestions and valued support.

I also extend my sincere thanks to all my friends and in particular to my project partners Miss Pallavi Suhasinee Behera, Miss Swagatika Bhoi, Miss Paradarshini Parida & Mr. Manoranjan Samal for the immense support and encouragement I received from them.

Saritarani Maharaj

DEDICATED TO MY PARENTS

ABSTRACT

A series of polymer electrolyte having Na^+ ion as the principal charge carrier has been prepared by solution casting technique and analyzed with different experimental techniques. In the present study, sodium iodide (NaI) was taken as the salt and poly (ethylene oxide), PEO was taken as the polymer host for polymer-salt complexation. Solution cast method was used to prepare polymer electrolytes of different polymer to salt ratio (O/Na= 0, 20, 40, 60, 80, 100). The structural characterization was carried out using X-ray diffraction. The XRD pattern showed the formation of polymer-salt complexation with the existence of both crystalline and amorphous phases in the materials. This semicrystalline nature of polymer electrolyte was observed by microstructural characterization using Scanning Electron Microscope. The electrical properties of polymer electrolytes were carried out using complex impedance analysis in the frequency range of 100 mHz to 1MHz at room temperature. Dielectric properties, a.c. conductivity and impedance data were analyzed with respect to different frequency and different compositions.

CONTENTS Page No.

CHAPTER 1

1.1 ELECTROLYTE:

Electrolytes are the substances which in their molten state or in aqueous solutions contain ions which are responsible to conduct electricity [1]. Electrolyte solutions are normally formed when a salt is dissolved into a polar solvent such as water and the individual components dissociate giving individual ions of salt by the process of solvation. For example

$$NaCl_{(s)} \rightarrow Na^{+}_{(aq)} + Cl^{-}_{(aq)}$$

1.1.1 Electrochemical devices:

It is the device in which chemical energy is converted into the electrical energy through oxidation and reduction processes. Basically, there are mainly two types of electrochemical cells. In one cell spontaneous reaction occurs (ex- galvanic cell); and in other non-spontaneous reaction occurs (ex- electrolytic cell). Both types of cells contain electrodes where the oxidation and reduction reaction happens. Oxidation occurs at the electrode termed as anode and the other one is cathode where reduction takes place. The anode of an electrolytic cell is positive (cathode is negative), since the anode collects anions from the solution. However, the anode of a galvanic cell is negatively charged, since the spontaneous oxidation at the anode is the source of the cell's electrons or negative charge. The cathode of a galvanic cell is its positive terminal. In both galvanic and electrolytic cells, oxidation takes place at the anode and electrons flow from the anode to the cathode. Till now in most of the electrochemical cells, liquid electrolyte is used.

1.1.2 Disadvantages of liquid electrolyte:

There are quite a few disadvantages of liquid electrolytes being used in these devices. The first disadvantage is leakage of electrolyte from the electrochemical devices. Further, the devices using liquid electrolytes are bulky and difficult to transport from one point to other i.e., it is not portable. These devices also possess low energy and power density. Adding to this, the troubles are the reaction between the electrodes and the electrolyte which gradually corrodes the electrodes. This ultimately decreases the lifespan of the device. The boiling point of the solvent used limits the temperature range of operation of the device. All these inconveniences posed by the liquid electrolytes paved the way for solid electrolytes.

Moreover, using the solid electrolyte; we can get more energy and power density even if minimizing the size of the devices. Hence the introduction of the solid electrolyte is not only eradicating these obstacles, but also gives rise to more benefits. The following section gives a brief discussion of the solid electrolytes, their properties and applications [2].

1.2 SOLID ELECTROLYTES:

Fast ion conductors possess a regular structure with immobile ions, and liquid electrolytes which have no regular structure in 3-D and fully mobile ions [3]. A solid electrolyte should have the following characteristics:

I. Ionic conductivity should be of very high (i.e., 10^{-1}-10^{-4} Scm^{-1}) at room temperature with negligible electronic conduction ($<10^{-6}$ Scm^{-1}).
II. The principal charge carriers should be ions only.
III. The activation energy (i.e.; energy require to initiate/activate the process) should be very low (< 0.3 eV) [4, 5].

Application:

i. Batteries
ii. Fuel cells
iii. Gas sensors
iv. Display devices

1.3 CLASSIFICATION OF IONIC CONDUCTORS:

Based on microstructure and physical properties the solid electrolytes can be classified into 4 types [3, 6];

(i) Frame work crystalline/polycrystalline materials
(ii) Amorphous glassy electrolytes
(iii) Composite or dispersed phase electrolytes
(iv) Polymer electrolyte

The above mentioned phases belong to either ordered or disordered materials. Among four except framework crystalline materials, all three are in disordered state. Furthermore, among these three phases, amorphous-glassy and polymer electrolytes are microscopically

disordered, whereas composite electrolytes are macroscopically disordered. The electrolyte we have studied for the present case is Polymer electrolyte.

1.4 POLYMER ELECTROLYTES:

Polymer electrolytes are a new class of solid ionic materials, which are usually formed by complexing polar polymers like PEO, PPO, PEG etc., with ionic salts of monovalent alkali metal salts [7].

Advantages of polymer electrolytes as compared to liquid electrolytes are;

- Excellent processability and design flexibility.
- Satisfactory mechanical properties, mechanical, thermal, electrochemical stability and an ability to form good electrode/electrolyte contact.
- Higher safety due the absence of flammable organic solvent.

For solid-state electrochemical device applications, the polymer electrolyte materials should possess the following properties:

- High ionic conductivity $\sigma \geq 10^{-4}$ Scm^{-1} at room temperature.
- High cationic transference number $t_{ion} \sim 1$.
- Good chemical, thermal, mechanical and electrochemical stabilities.
- Good compatibility with the electrode materials.
- Low activation energy with temperature for ionic conduction.
- No phase change in the operating temperature regime
- Low glass-transition temperature (T_g) for ionic conductivity

Due to the above excellent properties of the polymers, the idea of using polymer electrolyte has been conceived by the scientific community in recent years.

For the preparation of polymer-electrolyte (i.e., polymer-salt complex), we have to consider the following characteristics while choosing the polymer and the salt.

(i) Polymer having atoms or groups with sufficient electron-donor have the ability to make coordinate bonds with cations

(ii) Low glass transition temperature (T_g) of polymer host.

(iii) Polymers with low cohesive energy density and high flexibility have the greatest tendency to interact with salts.

(iv) The salts having low lattice energy are most likely to form polymer salt complexation. These salts usually contain univalent alkali ions with larger anions (e.g., $CF_3SO_3^-$, I^- , ClO_4^- , HPO_4^- etc).

1.5 STRUCTURE AND MORPHOLOGY OF POLYETHYLENE OXIDE:

Polyethylene oxide (PEO) is one of the most studied polymer host for polymer electrolyte preparation. Although PEO-based polymer electrolyte exhibits sufficient mechanical properties to act as a separator in a cell, the electrical conductivity, electrochemical & transport properties are inferior and needs improvement. The poor conductivity is linked to the crystalline nature and to the restrictive segmental motion of the PEO especially the high molecular weight PEO [5,16]. PEO is a semi crystalline material with about 70-85% crystallinity and amorphous elastomeric phase at room temperature. Due to partial crystallinity in the structure the problem arises both at microscopical and macroscopical level. The form of the polycrystalline phase is often dendritic or spherulitic crystalline structure with well separated amorphous boundary. The gross morphological structure of PEO-salt complexes may play an important role in determining the ion transport properties of the material. PEO is a linear polymer and the regularity of the unit is - $(CH_2$-CH_2-O) -. The melting point, T_m of the crystalline phase is 65°C and the glass transition temperature, T_g of the amorphous phase is – 60°C.

1.6 LITERATURE SURVEY:

1.6.1 The research work on polymer electrolyte dates back to the pioneering work of Wright and co-worker, who first reported the ionic conduction in poly–ethylene oxide (PEO) and alkali metal salt complexation. Later Armand explored the potential applications of these materials for device applications. [18].

1.6.2 Michel Armand reported that the conduction in polymer electrolyte is mainly in the amorphous domains as compared to crystalline domain [19].

1.6.3 B. Scrosati et al gave the idea about the physical and chemical properties of a new class of lithium conducting polymer electrolytes formed by dispersing ceramic powers at the nano scale size into a PEO-$LiClO_4$ complex. [20].

1.6.4 M. A. Ratner experimentally described about the ionic conductivity of solid (polymer) electrolyte which is much higher than that of traditional ionic solids such as NaCl which lies in the range of 10^{-6} to 10^{-1} S/cm [21].

1.6.5 Amrtha Bhide et al reported a conduction characteristics free standing flexible electrolyte films of composition $(PEO)_6$:$NaPO_3$ +x wt %- PEG_{400} $(30 \leq x \leq 70)$. A combination of X-ray diffraction (XRD), optical microscopy, differential scanning calorimetry (DSC) studies provided the information about the enhancement in the amorphous phase of polymer due to the addition of plasticizer. A reduction in the glass transition temperature also observed from the DSC technique indicating an increase in the flexibility of the polymer chain. Determination of cationic transport number (t_{Na^+}) of 0.42 confirmed the ionic nature of the polymer electrolyte [22].

1.6.6 M. A. G. Marttins reported the behavior of a series of polymeric electrolytes, formed by poly (ethylene oxide) and salts of divalent metals. Finally they concluded that the conductivity of divalent polymer electrolytes depends on several factors, such as nature of the anion, nature of the cation, stoichiometry and thermal history of the complex, preparation conditions and temperature [23].

1.6.7 Papke et al suggested that strong cation-oxygen interaction energies provide the driving force for conformational changes of the polymer. Apart from these they pointed out the factors upon which ionic transport depend i.e. the multiple associations of carrier ions to polymer segments, the segmental motion with associated ions, and the dissociation of salt [24].

1.6.8 R. S. Agrawaal et al overviewed some possible theoretical models suggested to understand the ion-transport mechanism in superionic systems. They took polyvinyl pyrrolidone (PVP) as their polymer host and $NaClO_4$ as salt to make polymer electrolyte, which was synthesized by solution cast technique. Dielectric spectroscopic studies were performed to understand the ion transport (conductivity) process in polymer electrolyte. [25].

1.6.9 F. Croce et al studied the electrochemical properties of lithium ion-conducting polymer electrolytes in terms of mechanical properties and of ionic conductivity at low temperature. [26].

1.7 **OBJECTIVES:**

The followings are the main objectives of our project work

(i) Synthesis of sodium ion conducting polymer electrolyte by solution cast technique
(ii) Structural characterization of polymer electrolyte by X-ray diffraction technique
(iii) Micro structural characterization using Scanning Electron Microscope (SEM)
(iv) To understand ion transport mechanism, electrical conductivity using Dielectric Spectroscopy will be studied.

1.8 ORGANIZATION OF THE THESIS:

This thesis consists of four chapters

Chapter 1:- This chapter gives a brief description of electrolyte, liquid electrolyte, solid state ionics, solid polymer electrolyte & structure of PEO. In addition to the literature survey, the main objectives of the work are also briefly described.

Chapter 2:- The different methods of preparation of polymer electrolyte and the adopted procedure are discussed along with the principle of different characterization techniques.

Chapter 3:- This chapter deals with the structural, micro structural characterization carried out by XRD, SEM. It also gives detailed studied of the electrical property of polymer electrolyte with the help of Impedance Spectroscopic Analysis at different frequency. The d. c. conductivity is calculated from the complex impedance plot.

Chapter 4:- Summary and conclusion of the present work is being explained.

CHAPTER 2

SAMPLE SYNTHESIS

2.1 DIFFERENT METHODS OF PREPARATION:

There are different methods of preparation of polymer electrolytes. Here we are describing some common methods of preparation.

Solution Casting Method: It is a simple and most commonly used method. By this method polymer thin films of varying thickness can be prepared. Generally, this method includes the following steps: (a) Polymer is dissolved in the solvent and allowed to be swollen, (b) Appropriate amount of salt is added to that polymer solution, (c) Mixing by means of magnetic-stirrer for complexation, (d) Addition of a specified amount of filler/plasticizer to the polymer solutions for high conductivity, (e) Casting the mixture on a glass plate/Petridish/substrate, (f) Lastly drying in vacuum or in an inert atmosphere.

Spin Coating: There, so many similarities in between spin coating method and the casting method. In this method, instead of casting the film on a substrate, the mixture is dropped on a substrate and placed in a spin coater that can be rotated at an adjustable rotation speed. The thickness of film can be controlled easily by maintaining the viscosity of the mixture and the speed of the rotation. However, this method is only applicable if the viscosity of the mixture is not appreciably high. For a gel mixture, the spin coater rotation is not enough to spread the mixture droplet to form thin film.

In the present study we have used solution casting method as it is relatively easier method for preparation of polymer electrolytes thin films.

2.2 PROCEDURE:

Preparation of polymer electrolyte based on PEO:

Appropriate amount of polymer host, polyethylene oxide (PEO) was taken in a conical flask and 20 ml acetonitrile (CH_3CN) added in the polymer. After swelling of polymer in the Acetonitrile medium, appropriate amount of salt, sodium iodide (NaI) was added in that solution. Then the solution was stirred for 10 hours by means of magnetic-stirrer. The obtained solution was then casted on separate petridish and allowed to evaporate slowly at room temperature. Free standing thin films of polymer electrolyte were obtained.

FLOW CHART:

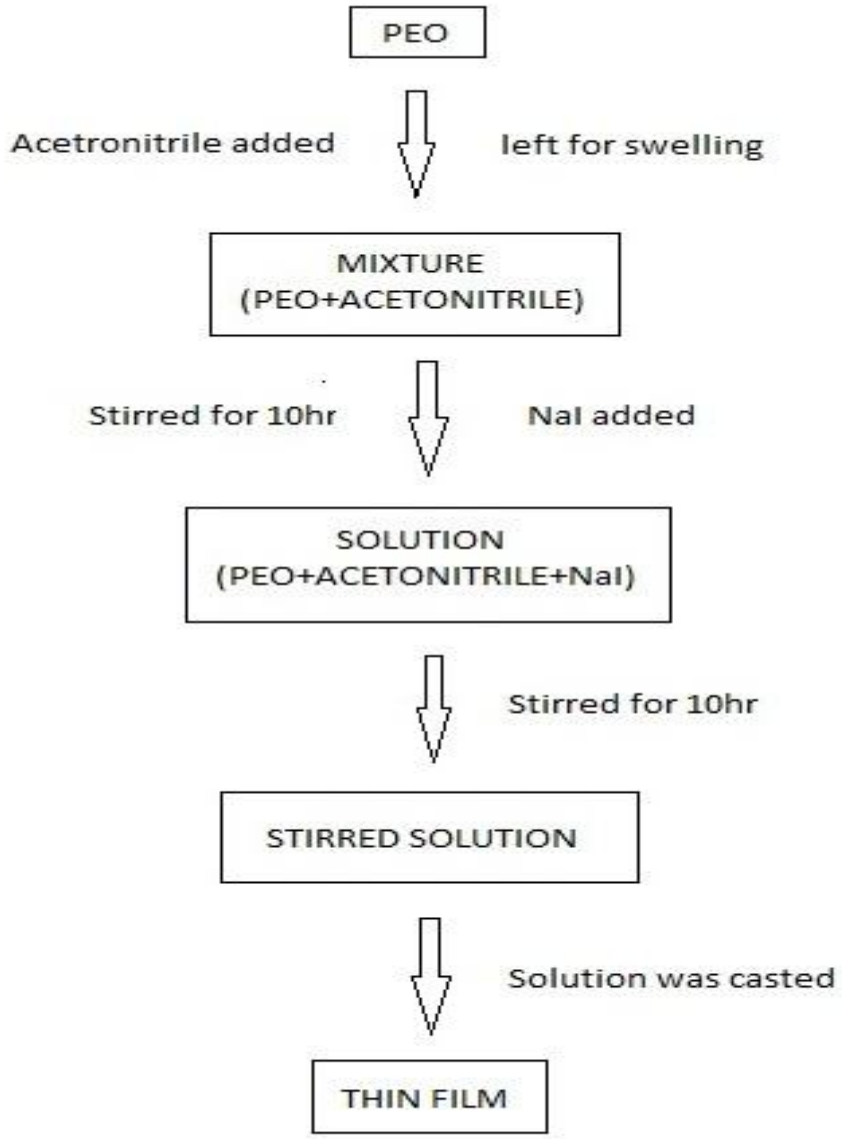


Fig. 2.1 Flow chart for preparation of polymer electrolyte

2.3 EXPERIMENTAL DETAILS

2.3.1 X-ray Diffraction (XRD):

The X-Ray diffraction studies are carried out to confirm the formation of the material and its phase identification. The accurate determination of inter-planar spacing, lattice parameters, crystallinity, various microstructural parameters etc. from XRD pattern, also provides an important basis in understanding the various physical properties of the materials [27]

Condition for Constructive interference (only when) $n\lambda=2d sin\theta$ i.e. it obey Bragg's law, where n is the order of diffraction, $\boldsymbol{\lambda}$ is the wavelength of Cu k_{α}, d is the inter planar spacings and θ is the angle of diffraction.

Application:

From XRD, we get the following results

1) The average spacings are measured between layers or rows of atoms
2) The orientation of a single crystal or grain can be determined.
3) The crystal structure (crystallinity) of unknown materials is obtained.
4) The size, shape of small crystalline regions is measured.

For structural characterization of the polymer, the XRD patterns of all the electrolytes have been recorded at room temperature (25°C) using Phillips X-ray powder diffractometer with radiation of λ = 1.5405 Å in a wide 2θ (Bragg angle) range ($10° \leq 2\theta \leq 40°$) at a scanning rate of 2°/min.

2.2.2 Scanning Electron Microscope (SEM):

The scanning electron microscopy (SEM) is a versatile tool to characterize microstructures of the samples. SEM makes use of point to point scanning of the solid surface, which produces a clear image of specimens, and provides information about their size which lies in the range of micro-meter. In a typical SEM, an electron beam is emitted from an electron gun fitted with a tungsten filament cathode. When the primary electron beam interacts with the sample, the electron loses energy by repeated random scattering and absorption by the specimen. The energy exchange between the electron beam and the sample results in the reflection of high-energy electrons by elastic scattering, emission of secondary electrons by inelastic scattering and the emission of electromagnetic radiation, each of which can be detected by specialized detectors [28].

The surface morphological studies of the material sample have been carried out using a computer-controlled scanning electron microscope (JEOL Scanning Electron Microscope, JSM-6480LV). Here the polymers were platinum coated prior to being scanned under high-resolution field emission gun scanning electron microscope. Surface morphology of different polymer to salt ratio (O/Na= 0, 20, 60, 100) for polymer electrolytes were obtained.

2.2.3 Dielectric Spectroscopy:

Complex impedance spectroscopy (CIS) is a most promising tool used mostly to characterize the microstructure and electrical property. It is based on analysis of the ac response of a system to sinusoidal perturbation and calculation of impedance (resistance for an ac circuit) as a function of frequency. This spectroscopy is also very effective to study properties of intragranular and interfacial regions and their interrelations, their temperature & frequency dependent phenomena in order to separate the individual contributions from the total impedance and their interfaces with electronically conducting electrode [29-30]. Also, it enables us to calculate the relaxation frequency, which is an intrinsic property of the sample, independent of its geometrical factors. Apart from these it also helps us to find

(i) ac and dc conductivity
(ii) Dielectric constant
(iii) Dielectric loss (tan δ)

The frequency dependence of various impedance parameters of a material can be described via the complex permittivity (ε^*), complex impedance (Z^*), complex admittance (Y^*), complex electric modulus (M^*) and dielectric loss or dissipation factor (tanδ). They are in turn related to each other as follows:

$\epsilon* = \varepsilon' - j\varepsilon''$ Where $\varepsilon' = \frac{-Z''}{\omega C_0(Z'^2+Z''^2)}$ and$\varepsilon'' = \frac{Z'}{\omega C_0(Z'^2+Z''^2)}$;

$M* = M' + jM'' = (1/\varepsilon') = j\omega\varepsilon_0 Z*;\ Z* = Z' - jZ'' = (1/jC_0\omega\varepsilon*)\ and \tan\delta = (\varepsilon''/\epsilon,) = \left(\frac{M''}{M'}\right) = \left(\frac{Z'}{Z''}\right) = \left(\frac{Y'}{Y''}\right)$ ($w = 2\pi f$ is the angular frequency, ' and " mark are the real and imaginary part of complex parameters ($\epsilon*, Z*, M*, Y*$), C_0 is the geometrical capacitance, j=$\sqrt{(-1)}$. These relations provide a wide scope for a graphical representation of different impedance parameters under various experimental conditions (i.e. temperature, frequency etc.). Here the complex impedance measurement were carried out using a computer-controlled impedance analyzer (PSM 1735 Impedance Analysis Package (Newton 4th Ltd.)) in the frequency range of 100 mHz to 1MHz at an a.c. signal level of 100 mV at room temperatures. The polymer electrolyte films were sandwiched between two stainless steel blocking electrodes for the electrical measurement.

CHAPTER 3

RESULTS AND DISCUSSION

3.1 X-RAY DIFFRACTION:

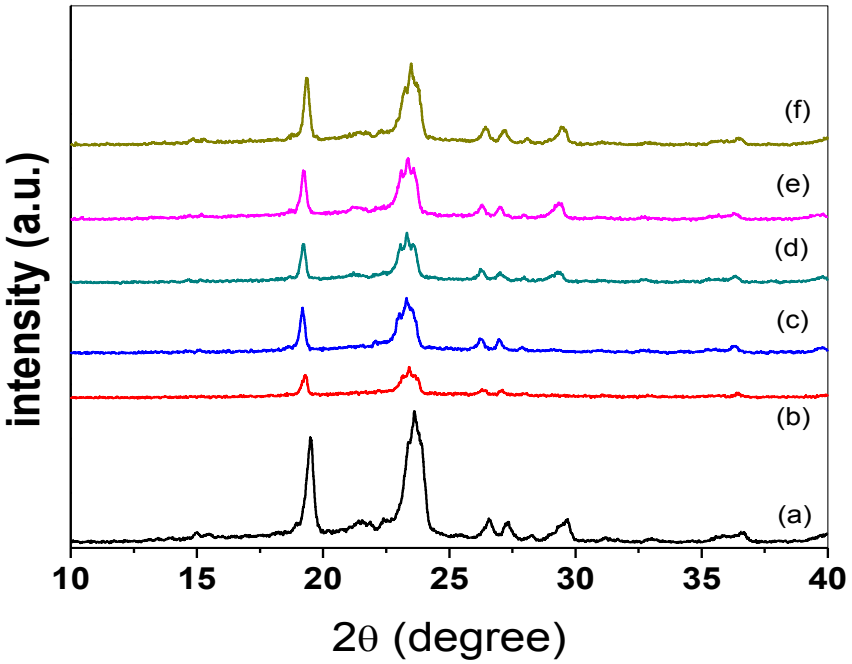


Fig3.1 XRD patterns of $(PEO)_X$-NaI (X=O/Na=0(a), 20(b), 40(c), 60(d), 80(e), 100(f))

Fig 3.1 depicts the XRD patterns of PEO and polymer electrolyte of different O/Na ratio. The XRD patterns showed the presence of few crystalline peaks and amorphous humps indicating the semi crystalline nature of all the polymer electrolytes. From the XRD patterns it is observed that, two Main peaks are appearing around 19^o and 23^o. The XRD pattern of polymer salt complexes is similar to that of the host PEO indicating the complexation of polymer with salt. Peak observed around 19^o shifting towards the low angle side with increase in O/Na ratio and for higher concentration reverse trend is observed.

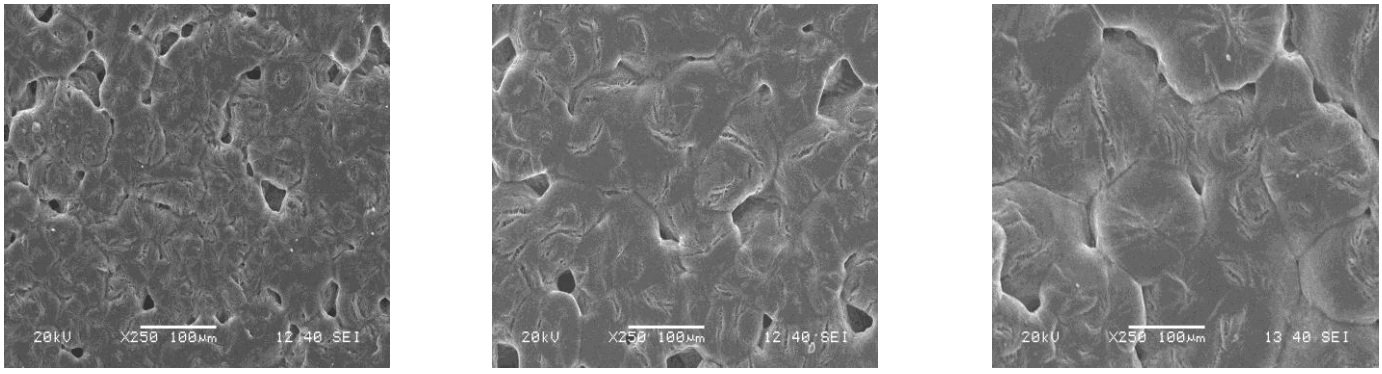
The inter-planar spacing was found using the Bragg's formula: $2d\sin\theta = n\lambda$, where, d is the inter-planar spacing, n is the order=1, here, the shifting of the peaks is observed at ~ 19^o, for which we have calculated all the structural parameters. The average crystallite sizes can be determined from the full width half maximum of the peak around 19^o using Scherer's formula given by: $D = 0.94\lambda/\beta\cos\theta$ Where, D is the crystallite size, λ is the wavelength of X-ray 1.5405 Å, β is the FWHM and θ is the diffraction angle of the strongest characteristic peak.

The calculated crystallite sizes and inter-planar spacing of PEO at different ratio (O/Na= 0, 20, 40, 60, 80, 100) for peak around 19^{o} are shown in the table 3.1.

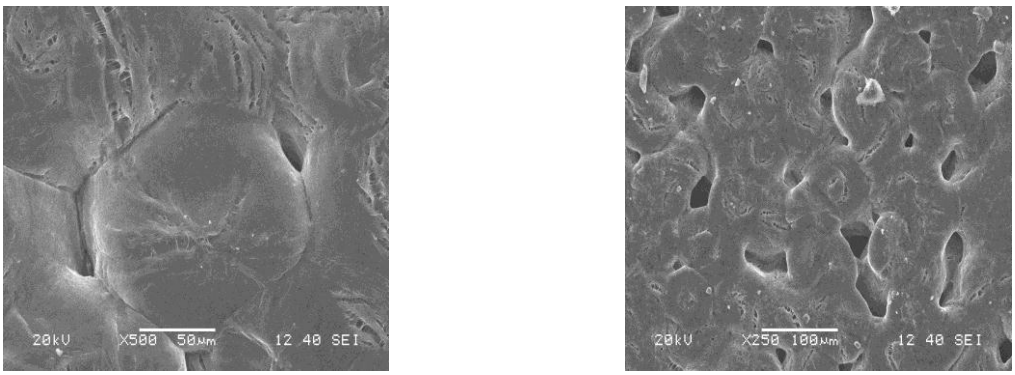
Table 3.1 calculation of inter-planarspacings and crystallite sizes

PEO concentration	2θ (in degree)	Interplanar spacing (d) (A^0)	Crystallite size (D) (nm)
PEO	19.49	4.5515	27
PEO_{20}-NaI	19.28	4.6028	35
PEO_{40}-NaI	19.18	4.6234	37
PEO_{60}-NaI	19.21	4.6160	37
PEO_{80}-NaI	19.23	4.6122	37.
PEO_{100}-NaI	19.35	4.5834	34

3.2 SCANNING ELECTRON MICROSCOPY ANALYSIS:



(a) **(b)** **(c)**



(d) **(e)**

Fig 3.2 SEM images for various O/Na ratio (a) O/Na=0, (b) O/Na=20, (c)O/Na=60, (d) O/Na=60, (e) O/Na=100

Fig 3.2 shows the Scanning Electron Micrographs (SEM) of PEO and polymer-salt complex with different O/Na ratio (O/Na=0, 20, 60, 100). The morphology of the above mentioned micrographs provide the information about the presence of distinct spherulites having characteristics lamellar microstructure. The region between spherulites boundaries deals with the amorphous phase. The micrographs give the idea of the crystalline nature of spherulite with amorphous boundary of the polymer electrolytes. There is no systematic change in the surface morphology with different polymer to salt ratio.

3.3 STUDY OF ELECTRICAL PROPERTY:

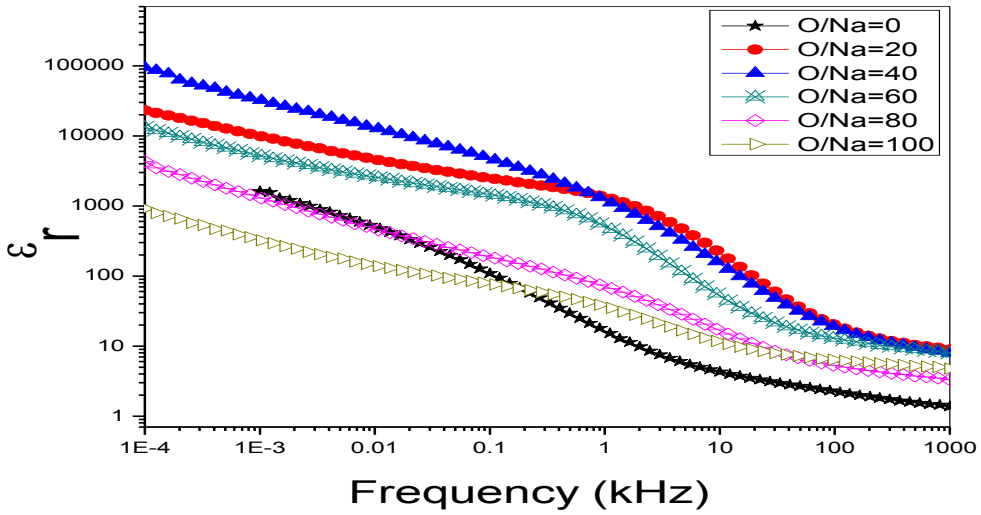


FIG 3.3 Variation of relative dielectric constant with frequency

Fig 3.3 shows the variation of dielectric constant with frequency of polymer electrolyte at different O/Na ratio (polymer to salt ratio). In all the cases, a strong frequency dispersion of permittivity is observed in the lower frequency region, whereas it is shows a nearly frequency independent behavior at higher frequency region irrespective of polymer to salt ratio. The decrease of dielectric constant with increase in frequency may be attributed to the electrical relaxation processes. The sharp decrease in the dielectric constant with frequency at the low frequency region indicates the presence of space charge polarization.

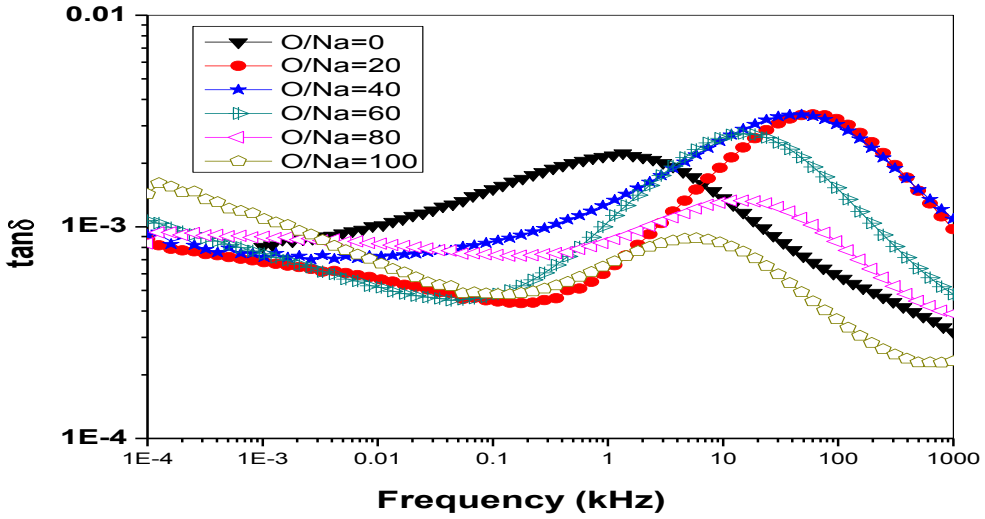


FIG 3.4 Variation of dielectric loss with frequency

Fig 3.4 shows the variation of tangent loss with frequency at different polymer to salt ratio for polymer electrolyte. The tangent loss spectra of all these samples are characterized by peaks appearing at a characteristics frequency for different O/Na composition suggesting the presence of relaxing dipoles in all the samples. On increasing frequency the tan δ peaks are shifted towards higher frequency side up to O/Na=40 and for higher O/Na ratio it decreases. The strength and frequency of relaxation depends on the characteristic property of dipolar relaxation.

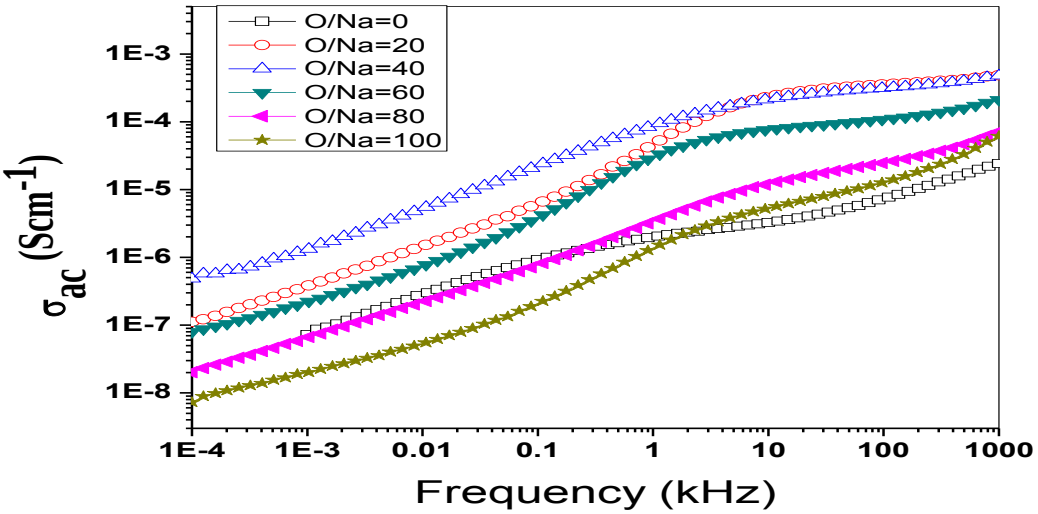


FIG 3.5 Variation of a.c. conductivity with frequency

Fig 3.5 shows the variation of a. c. conductivity with frequency of the material. The a. c. conductivity was calculated using measured dielectric parameters using the relation; $\boldsymbol{\sigma_{ac} = \omega\varepsilon_r\varepsilon_0 tan\delta}$, where $\boldsymbol{\omega = 2\pi f}$, is the angular frequency, ε_0 is the permittivity of the free space. The ac conductivity pattern indicates a progressive rise in ac conductivity with increase in frequency up to a certain frequency and further increasing in frequency it remains constant. The observed frequency independent plateau in the high frequency represents d. c. conductivity of the material.

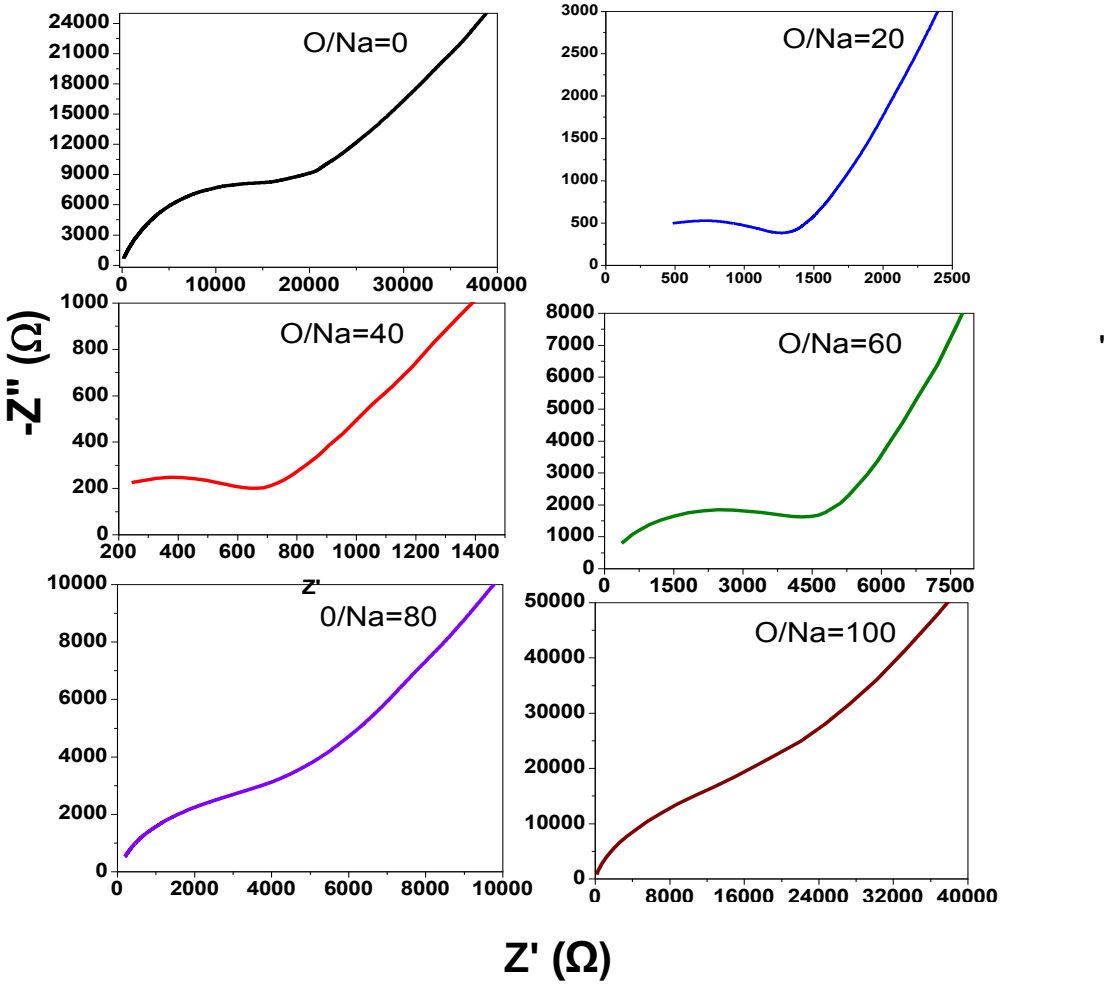


FIG 3.10 Complex Impedance spectra of PEO_x-NaI (x= 0, 20, 40, 60, 80, 100)

Fig 3.10 shows the complex impedance spectra of PEO-NaI complex with different values of O/Na (i.e. x=O/Na=0, 20, 40, 60, 80, 100). The typical complex impedance spectra (i.e., Nyquist Plot) of the samples comprises of a broadened semicircle in the high frequency and a spike in the low temperature region for all polymer to salt ratio. The high frequency semicircle has been attributed to the bulk properties of the material which arises due to the parallel combination of bulk resistance (R_b) and bulk capacitance (C_b) whereas the low

frequency spike arises due to the material-electrode interface of the material. The intercept of the semicircle arc on the real axis gives the bulk resistance of the electrolyte. The d.c. electrical conductivity (σ_{dc}) of the material was calculated from the complex impedance spectrum using the relation

$\boldsymbol{\sigma_{dc} = \frac{1}{R_b}\frac{t}{A}}$ Where R_b is the bulk resistance, t is the thickness and A is the area of the sample.

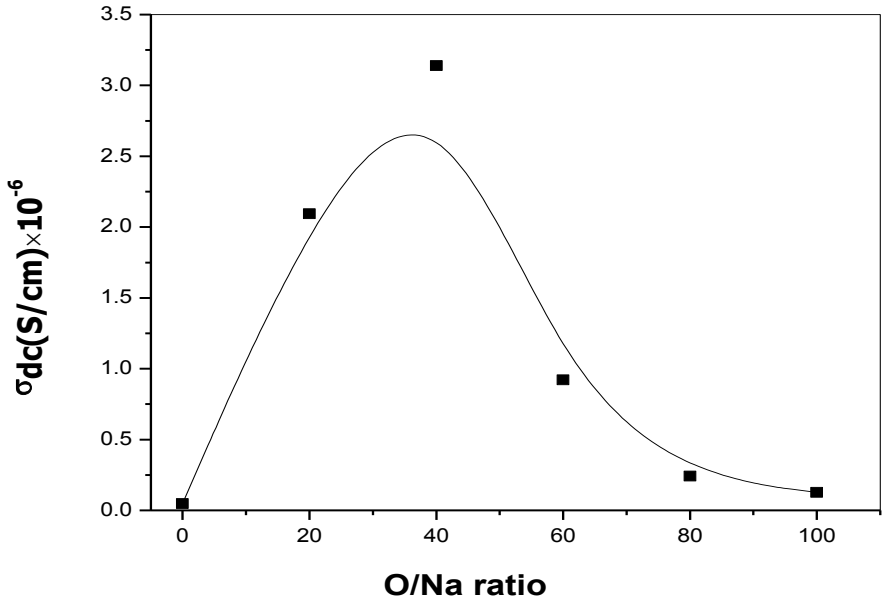


Fig. 3.11 Variation of d.c. conductivity (σ_{dc}) with different O/Na ratio (O/Na=0, 20, 40, 60, 80, 100)

Fig 3.11 shows the variation of d.c. conductivity (σ_{dc}) with different O/Na ratio (i.e. O/Na=0, 20, 40, 60, 80, 100). From the graph it has been observed that the d.c. electrical conductivity increases with increase in polymer to salt ratio and attains a maximum value for O/Na=40. On and above O/Na=40 the d.c. conductivity decreases monotonically.

CHAPTER 4

SUMMARY & CONCLUSIONS

Poly(ethylene oxide), PEO as polymer host and sodium iodide, NaI as salt have been taken as starting materials to prepare polymer electrolyte by solution cast method with different O/Na ratio (O/Na=0, 20, 40, 60, 80, 100). The structural, morphological and electrical properties of the polymer electrolyte have been studied with different experimental techniques. The result obtained can be concluded as follows:

1. The complexation of the polymer electrolyte has been studied using XRD analysis. The crystallite size (using Scherer's formula) and the interplannar spacing (using Bragg's law) of the polymer electrolytes were calculated from the XRD data.
2. By scanning electron microscope, the morphological structures of polymer electrolytes were analyzed. It provided the information about the existence of crystalline and amorphous phases of polymer electrolytes i.e. it confirmed the semi crystalline nature of polymer electrolytes.
3. The electrical properties of polymer electrolytes were studied by Complex Impedance Spectroscopic technique at different frequency ranging from 100 mHz to 1 MHz. a.c. and d.c. conductivity of the polymer electrolytes have been calculated from dielectric data and from Complex Impedance plot.
4. We found that for O/Na=40 composition, the electrolyte showed highest conductivity among all.

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